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VAPOR PRESSURE MEASUREMENT WITH DIFFERENTIAL THERMAL ANALYSIS: AN IMPROVEMENT IN THE METHOD

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A method is described that extends the temperature range over which vapor pressure may be measured when using differential thermal analysis. The technique developed allows for measuring vapor pressure of pure liquids that boil below room temperature.

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PREFACE

The work described in this report was authorized under Project No. 1C162622A553I, CB Simulants, Survivability and Systems Science. This work was started in November 1988 and completed in February 1989.

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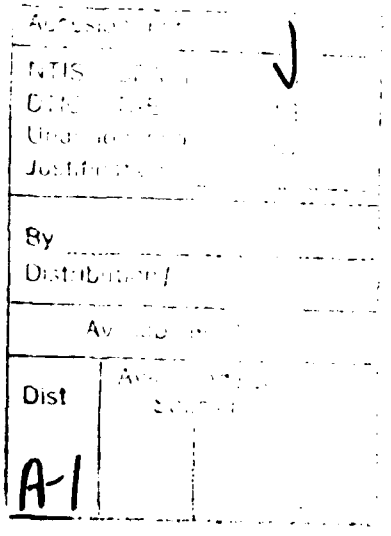

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VAPOR PRESSURE MEASUREMENT WITH DIFFERENTIAL THERMAL ANALYSIS: AN IMPROVEMENT IN THE METHOD

1. INTRODUCTION

The use of differential thermal analysis (DTA) to measure vapor pressure of pure liquids has been described in the open literature by Vassallo and Harden,[1] Chiu,[2] Kemme and Kreps,[3] and Krawetz and Torrog[4] and internally by Belkin and Brown.[5] Basically, all the references cite the same techniques and instrumentation. The DTA technique requires a small sample size (0.02 μl/data point) and permits rapid determination of the entire vapor pressure versus temperature curve (ca. 10 min/data point) from 10 to 760 torr. For these reasons, the DTA method is frequently preferred over other techniques (e.g., the Knudsen effusion method or isoteniscope, which require a greater sample volume and are much more time consuming) that are used in the U.S. Army Chemical Research, Development and Engineering Center laboratories. The references cited above describe measurement of vapor pressures of compounds that boil above room temperature. The method described in this report extends the temperature range for measuring vapor pressure by DTA to the subambient region.

2. EXPERIMENTATION

A DuPont Model 9900 Thermal Analyzer (DuPont Company, Wilmington, DE) was used in these experiments. The basic setup has been described previously.[1,3] The major differences between this procedure and those used by Vassallo and Harden[1] and Kemme and Kreps[3] were the use of a computer to control data acquisition and the employment of a Quick Cool sample holder accessory (DuPont Company). The Quick Cool accessory is a Dewar flask designed to hold the sample cell block, which allows for rapid cool down of the cell block and for subambient operations through the use of liquid nitrogen. The instrument was calibrated using triple distilled, deionized water, Freon 113 (trifluorotrichloroethane) and Freon 114 (1,2-dichloro-1,1,2,2-tetrafluoroethane). The pressure readout device was a Wallace and Tiernan Type 187 absolute manometer (Wallace and Tiernan, Belleville, NJ) capable of reading to the nearest 0.1 mm Hg.

2.1 Temperature Control.

Prior to measuring vapor pressures at very low temperatures, the ability of the DTA to control the rate of

temperature increase was investigated. Kemme and Kreps[3] had determined that 5 deg/min was the optimum heating rate for determining the boiling point. Therefore, it was critical that the cooled cell block did not self-warm at a faster rate. The cell block was cooled to -180 °C and allowed to self-warm. Figure 1 is a plot of the rate of temperature increase with time. The observed temperature rise was well below the desired 5-deg/min heating rate and, therefore, presented no problems.

2.2 Sample Handling.

To load samples that boil below room temperature into the glass capillaries that are placed in the sample cell block, special handling techniques were developed. The compounds that boil below room temperature are normally received in lecture bottles (LB) equipped with valves. The samples are transferred from the LB to a Reacti-Vial (Pierce Chemical Company, Rockford, IL) that is equipped with a screw cap containing a rubber septum. The vial is precooled to a temperature below the boiling point of the compound under study, and a portion of the sample is transferred from the LB to the vial. Once a sufficient amount of sample has been collected, the vial is capped. The sample in the vial will remain a liquid as long as the cap does not leak. Transferring the sample to the DTA glass capillary tube is accomplished by cooling the cell block with the capillary in place and transferring the proper amount of liquid using a precooled microsyringe.

3. DISCUSSION

The technique developed allows one to establish a complete vapor pressure-temperature curve (10-760 mm Hg) in less than 2 hr with a minimum of sample size. Plots of the vapor pressure versus temperature for Freons 113 and 114, respectively, are shown in Figures 2 and 3 where the symbols are experimental points, and the line is the calculated vapor pressure from the literature.[6,7] Tables 1 and 2 show the experimental temperatures and pressures compared with the calculated literature temperature at each experimental pressure. The data clearly indicate that the technique is quite good, giving data that agrees quite well with published values.

Representative thermograms are shown in Figures 4 and 5 as an example of output from the system.

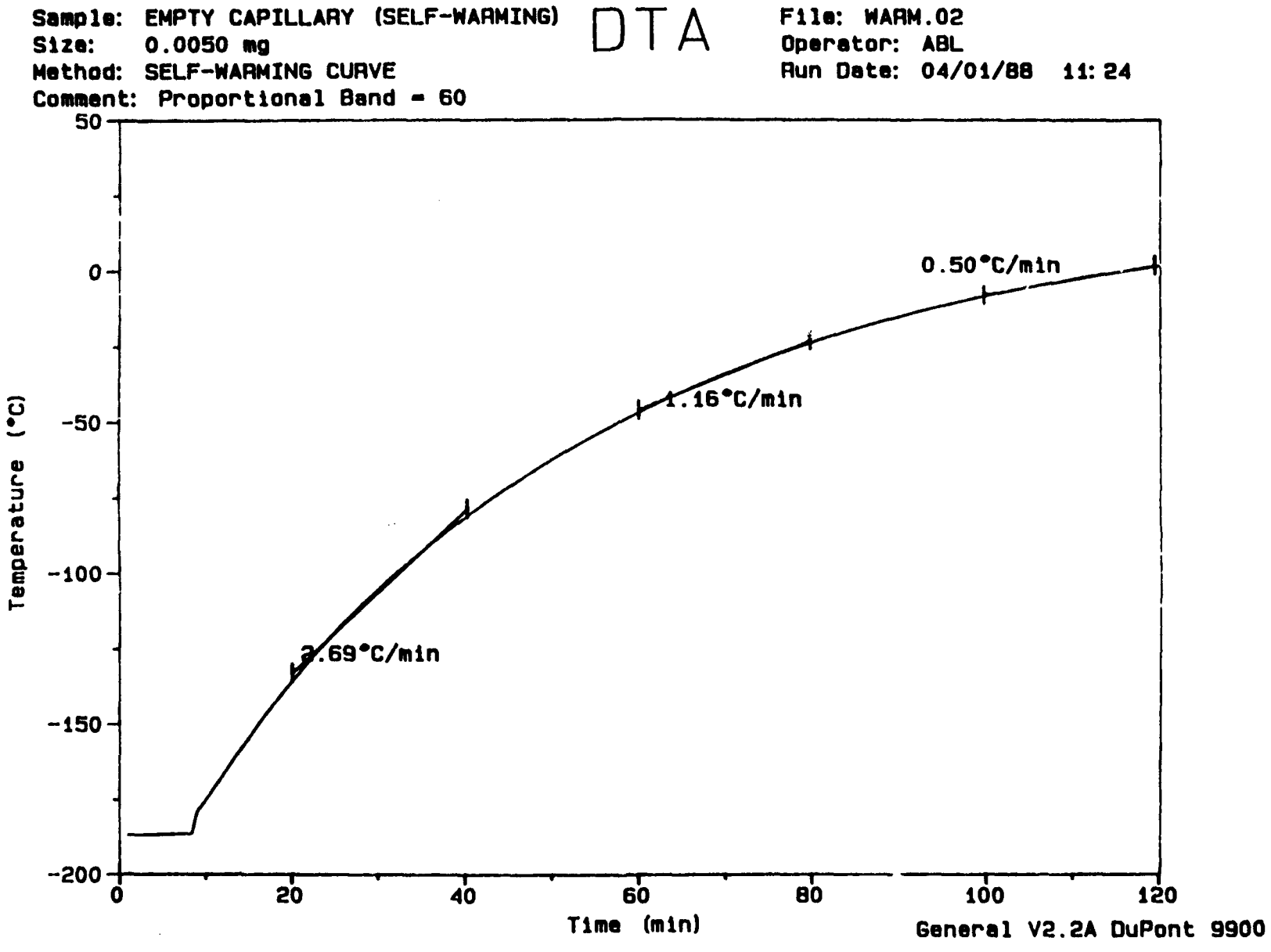

Figure 1. DTA Cell Block Self-Warming Curve

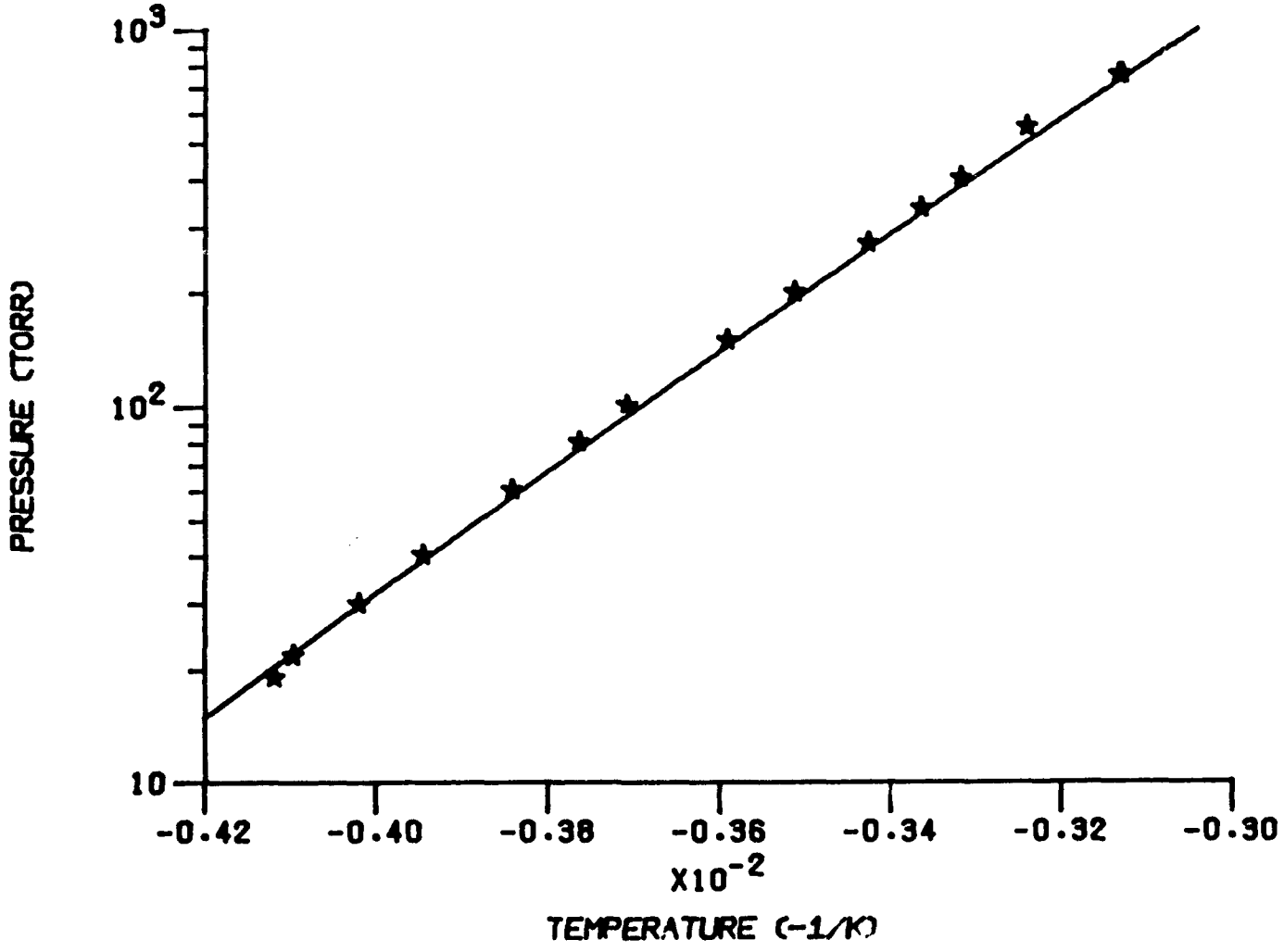

Figure 2. Vapor Pressure of Freon 113: Literature vs. Experimental

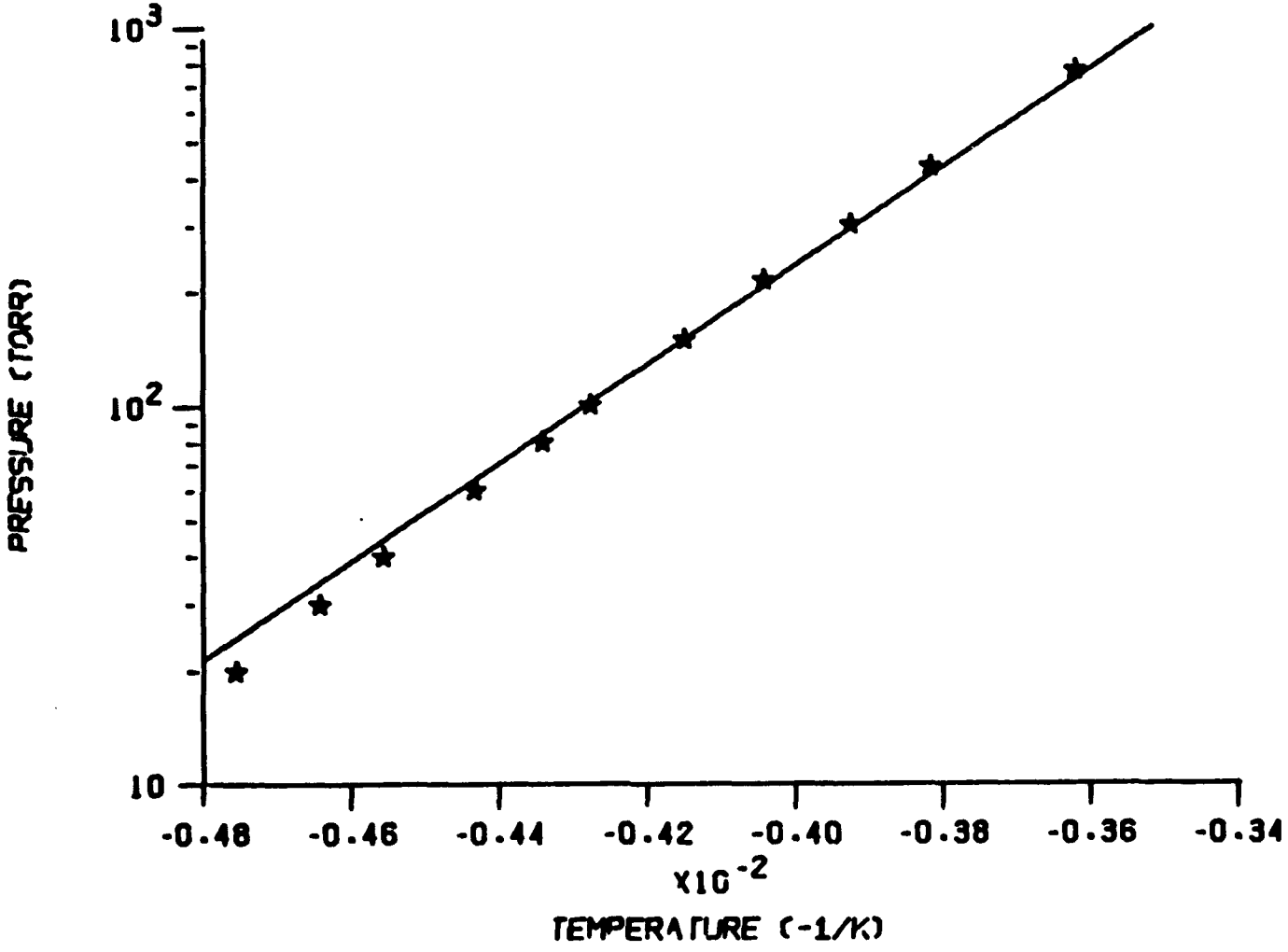

Figure 3. Vapor Pressure of Freon-114: Literature vs. Experimental

Table 1. Vapor Pressure Data for Freon-113

Temperature (°C)		Δt	Pressure
Experimental	Literature	(Lit - Exp)	(torr)
46.8	47.6	0.8	761.4
46.3	47.5	1.2	759.1
46.3	47.5	1.2	759.0
35.7	38.2	2.5	549.3
28.4	29.6	1.2	400.0
24.2	25.1	0.9	334.8
18.7	19.8	1.1	270.0
11.6	12.8	1.2	200.1
5.3	6.3	1.0	150.0
-3.4	-2.1	1.3	100.0
-7.4	-6.5	0.9	80.0
-12.8	-12.0	0.8	60.0
-19.7	-19.1	0.6	40.2
-24.3	-24.1	0.2	30.0
-29.0	-29.2	-0.2	21.9
-30.3	-31.3	-1.0	19.1

Table 2. Vapor Pressure Data for Freon-114

Temperature (°C)		Δt	Pressure
Experimental	Literature	(Lit - Exp)	(torr)
3.1	3.3	0.2	767.3
-11.2	-11.0	0.2	424.1
-18.4	-17.8	0.6	300.0
-25.8	-25.9	-0.1	213.2
-32.2	-32.2	0.0	149.2
-39.2	-39.7	-0.5	100.0
-42.8	-43.7	-0.9	80.0
-47.6	-48.6	-1.0	60.0
-53.6	-55.3	-1.7	40.0
-57.7	-59.7	-2.0	30.0
-62.8	-65.8	-3.0	19.9

4. CONCLUSIONS

A modified DTA technique for measuring vapor pressure has been shown to be a quick, easy method, requiring a very small sample. The use of a Quick Cool accessory extends the use of the method to subambient temperature region.

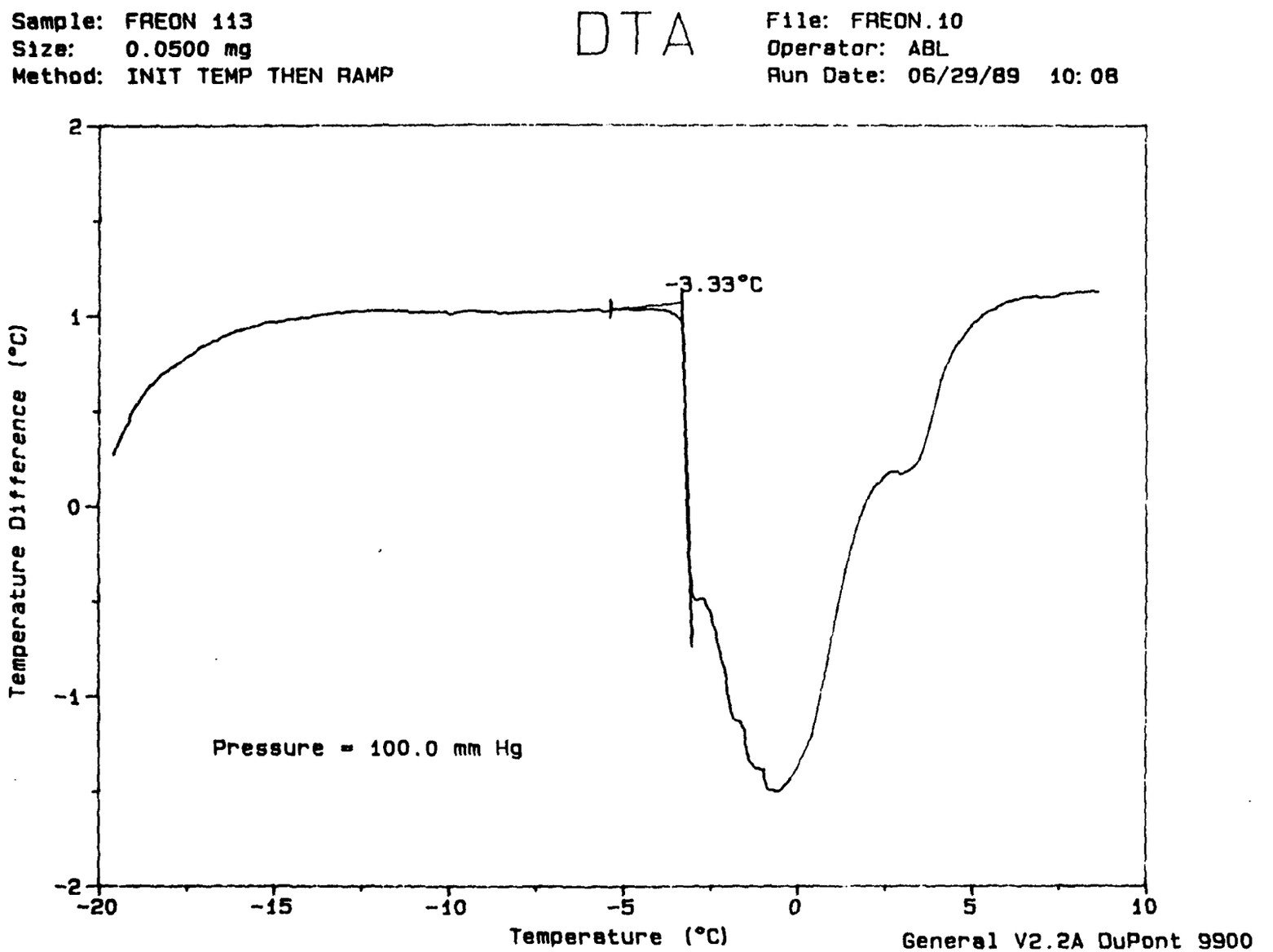

Figure 4. Boiling Thermogram for Freon-113

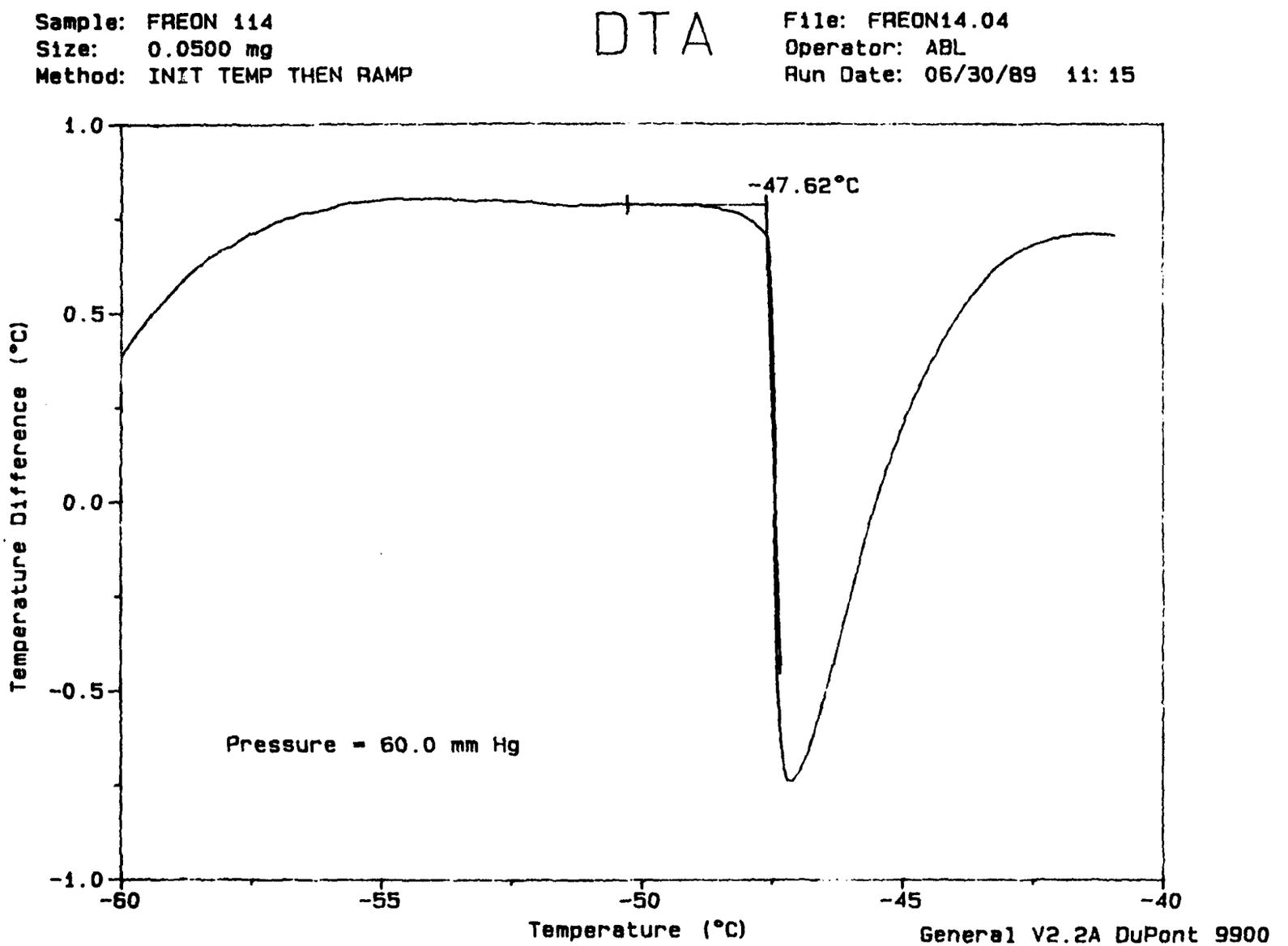

Figure 5. Boiling Thermogram for Freon-114

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